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(U) A REVIEW OF RECENT COMPATIBILITY

AND STABILITY STUDIES ON

HYDRAZINIUM DIPERCHLORATE

RAYMOND E. FOSCANTE

CAPT, USAF

TECHNICAL REPORT AFRPL-TR-69-46

MARCH 1969

AIR FORCE ROCKET PROPULSION LABORATORY

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

EDWARDS, CALIFORNIA

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AIR FORCE ROCKET PROPULSION LABORTORY

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EDWARDS, CALIFORNIA

FOREWORD

Numerous catastrophic failures of solid propellant motors incorporating HP-2 as the oxidizer suggest that certain important aspects of HP-2 reactivity, stability and combustion are not well understood.

It is the purpose of this report to organize and present the results of some fundamental investigations which shed considerable light on the characteristics of HP-2 propellants and the problems encountered in their development. In particular, the report reviews some recent compatibility and stability studies of HP-2 and relates the data obtained from these studies to observed motor test phenomena. This work was done under Project 314804ACP, and covers the period 1 July 1968 to 1 September 1968, with Dr. F. Q. Roberto as project engineer.

Responsibility for the validity of the contents resides in the author and his organizational element of the AFRPL.

Reviewed and approved for publication by:

W. H. EBELKE
Colonel, USAF
Chief, Propellant Division
Air Force Rocket Propulsion Laboratory

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UNCLASSIFIED ABSTRACT

Recent developments in hydrazinium diperchlorate (HP-2) chemistry are reviewed and related to solid propellant behavior. The reactions of HP-2 with model compounds and actual propellant ingredients are discussed with special attention paid to those interactions leading to gas generation, homopolymerization of binder components, oxidizer decomposition, cure reaction inhibition, and cure linkage destruction. The details of studies on the compatibility of HP-2 with NF systems are reviewed and conclusions reported. These fundamental chemical observations are then discussed in terms of large motor behavior.

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GLOSSARY OF TERMS

(U) HP   — hydrazinium monoperchlorate $(N_2H_4 \, HClO_4)$

(U) HP-2   — hydrazinium diperchlorate $(N_2H_4 \, 2HClO_4)$

(U) HN   — hydrazoic acid

(U) R-45M   — hydroxyl-terminated polybutadiene,
                  Sinclair Petrochemicals

(U) PBEP   — poly 1,2-bis (difluoramino) 2,3-epoxypropane
                  Shell Development Company

(U) Telagen CT — carboxyl-terminated polybutadiene
                  General Tire & Rubber Company

(U) GLC   — gas-liquid chromatography

(U) EPR   — electron paramagnetic resonance spectroscopy

(U) NMR   — nuclear magnetic resonance spectroscopy

(U) IR   — infrared spectroscopy

(U) HF   — hydrogen fluoride

(U) HCN   — hydrogen cyanide

(U) HNF_2 — difluoramine

(C) P-FABDE   — poly 1,4-bis (tris(difluoramino)methoxy)butene
                  oxide-2,3)

(U) AP   — ammonium perchlorate (NH_4ClO_4)

(U) HAP   — hydroxylammonium perchlorate $(NH_2OH \cdot HClO_4)$

(C) TVOPA   — tris vinoxypropyl adduct

$$\begin{cases} CH_2-OCH(NF_2)CH_2NF_2 \\ CH\ -OCH(NF_2)CH_2NF_2 \\ CH_2-OCH(NF_2)CH_2NF_2 \end{cases}$$

SECTION I
INTRODUCTION

(U)   Hydraziniu:n diperchlorate (HP-2) has been the subject of con-
siderable development as a solid propellant oxidizer.   Despite success-
ful formulation and scale-up of HP-2/hydrocarbon propellant formulations,
numerous instances of catastrophic motor failures have been reported and
the combustion behavior of HP-2 propellants has been both erratic and
irreproducible(1).   To date there has been no satisfactory explanation for
this behavior.

(U)   A review of the literature reveals that until recently a serious
gap existed in the understanding of those areas of the chemistry of HP-2
which ultimately determine its utility as a propellant ingredient.   There
was, indeed, little knowledge available concerning the chemical behavior
of HP-2 in the propellant environment during the various stages of the
porpellant's operational lifetime.

(U)   The purpose of this report is to review recent developments in
the area of HP-2 chemistry and to relate them to observed and predicted
propellant phenomena.

SECTION II
PROPELLANT STABILITY

(U) The incorporation of a new ingredient into a propellant system presents many problems which cannot be elucidated or resolved by a motor development effort. For example, the latter will not define the source of problems related to the thermal stability of the propellant and the compatibility of its components. The chemical and thermal behavior of components is, however, fundamental to the combustion performance, machanical behavior, curing characteristics and storage lifetime of the system.

(U) The adequacy of a propellant's stability depends upon the answers to several fundamental questions:

1. Are the components sufficiently stable to survive processing conditions without any significant chemical or physical changes?

2. Are the ingredients sufficiently unreactive with the curing functionalities so as not to interfere with the curing reaction?

3. Under storage conditions, will chemical inertness prevail or will oxidation or side reactions destroy the mechanical and physical integrity of the propellant system?

4. Once the reactivities of the components have been defined, do they pose insurmountable obstacles to successful formulation and operational usage of the propellant?

SECTION III

HP-2 STABILITY

(U) The key to the reactivity of hydrazinium diperchlorate with organic binder components lies in its acidity. One of the perchloric acid molecules is bonded in the salt rather loosely, as evidenced both from thermal decomposition data and by the fact that one hydroperchlorate titrates as a strong acid in water.

(U) The first step in the decomposition of HP-2 is the dissociation to free perchloric acid and hydrazinium monoperchlorate(2, 3, 4).

$$N_2H_6(ClO_4)_2 \longrightarrow N_2H_5ClO_4 + HClO_4$$
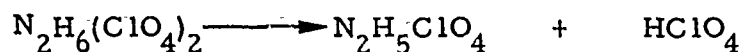
(U) This step has been verified by the isolation of anhydrous perchloric acid as the only vapor phase species in the initial stages of reaction(2, 3). In addition, flash pyrolysis mass spectrometric decomposition studies have shown the degradation of HP-2 to occur in two distinct stages(4). On a time scale, perchloric acid is the major initial decomposition peak, rising to a maximum. The second increase in perchloric acid intensity is accompanied by the fragmentation pattern characteristic of HP decomposition. A similar study of HP-2 was accomplished by Goshgarian(5) under conditions which allowed for the isolation and identification of HP as the solid remaining after initial perchloric acid loss. In both studies, hydrazoic acid, in addition to hydrazine and perchloric acid, was observed among the products. The relative amounts of these three compounds were dependent on experimental conditions. In Goshgarian's work, fragment detection was slower than in Hammond's method(4), due to the more distant location of the reactor and ion source. Hence, when more time is allowed for oxidation of hydrazine by perchloric acid, a greater amount of the hydrazoic acid is observed.

(U) Grelecki and Cruice(2, 3) have reported that after dissociation occurs to the monoperchlorate and free perchloric acid, the latter decomposes since it is considerably less stable than either HP or HP-2.

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(U) Levy(6) has shown that the nature of the decomposition of anhydrous perchloric acid is dependent on temperature. At relatively high temperatures (above 300°C), the decomposition of the acid is homogeneous; below this temperature, the reaction is heterogeneous, the rate being a function of the nature of the contacting surface. Levy(6) has also calculated the activation energy for the low-temperature decomposition of perchloric acid to be 22.2 Kcal/mole.

(U) Grelecki and Cruice(2,3), utilizing a manometric technique, have reported a value of 23.5 Kcal/mole as the activation energy for HP-2 decomposition between 100° and 150° C. Hammond (4) has calculated a similar value of 23 Kcal/mole for the HP-2 decomposition process from mass spectral data.

(U) The close similarity of the activation energies for HP-2 decomposition and that for perchloric acid indicate the rate-controlling step to be decomposition of the free acid(2,3). This conclusion has a further implication concerning the autocatalytic nature of the HP-2 decomposition process because perchloric acid decomposes heterogeneously as follows(6):

$$HClO_4 \longrightarrow HO^{\cdot} + {}^{\cdot}ClO_3 \qquad (2)$$
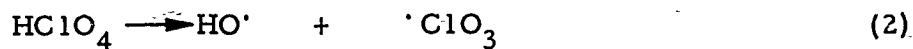
The oxidizing species formed can then attack the hydrazine moiety of HP-2, oxidizing it to ammonia and liberating another mole of perchloric acid. The newly formed acid then undergoes decomposition and repeats the process. Each mole of perchloric acid liberated has the capacity to oxidize seven moles of hydrazine. These, in turn, release seven more moles of acid.

(U) A chain-branching behavior can account for the autocatalytic nature of HP-2 decomposition, that is, the induction period and the rapid transition from this phase to a very fast acceleration of decomposition. The reactions proposed for the branching effect are listed below(2,3).

$$HO^{\cdot} + N_2H_5ClO_4 {\cdot} HClO_4 \longrightarrow H_2O + 1/2N_2 + NH_4ClO_4 + HClO_4$$

$${}^{\cdot}ClO_3 + 6N_2H_5ClO_4 {\cdot} HClO_4 \longrightarrow 3H_2O + 3N_2 + 6NH_4ClO_4 + 1/2Cl_2 + 6HClO_4$$

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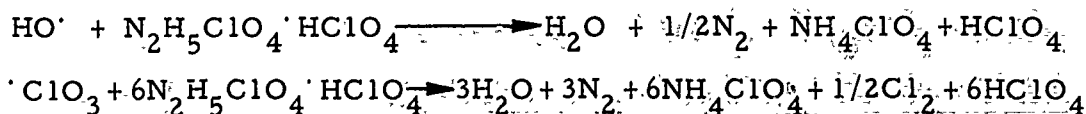
This explanation is also consistent with the stability observed for the monoperchlorate and the fact that, unlike HP-2, it does not undergo accelerated decomposition.

$$N_2H_5ClO_4 + \cdot OH \longrightarrow H_2O + NH_4ClO_4 + 1/2 N_2$$

$$7 N_2H_5ClO_4 + \cdot ClO_3 \longrightarrow 3 H_2O + 6 NH_4ClO_4 + 3 1/2 N_2 + NH_4Cl + HClO_4$$

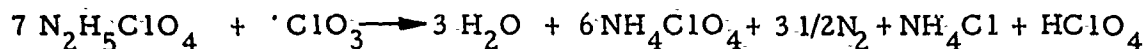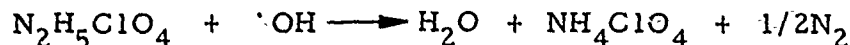It should be noted that the above results were obtained under experimental conditions which approximate propellant matrix conditions. That is, free perchloric acid remains in contact with the oxidizer and is therefore capable of initiating the acceleratory type of decomposition. In the mass spectrometric decomposition studies, degradation species do not remain in contact with the sample. Hence, the decomposition under the latter conditions is sequential and can be studied as such.

(U) In summary, hydrazinium diperchlorate is an acid-base salt consisting of a stable perchlorate salt (HP) to which a second perchloric acid moiety is loosely bonded. The decomposition of HP-2 is a two-stage reaction in which the first step is the "easy" loss of the loosely held acid moiety to give HP and anhydrous perchloric acid. Henceforth, the rate of the reaction is controlled by perchloric acid decomposition. The generation of oxidizing species from degradation of the latter makes the reaction autocatalytic. The existence of the induction period is a fact of special signigicance for predicting propellant storage behavior.

(U) Hydrazoic acid has been noted among the decomposition products from HP-2(4, 5), a significant observation from a hazards standpoint. The overall decomposition scheme for hydrazinium dperchlorate is one of increasing sensitivity. HP-2 dissociates to the monoperchlorate, a more sensitive material, which, in turn during its own degradation, can give an even more hazardous compound, hydrazoic acid.

SECTION IV
HP-2 COMPATIBILITY

(U) From a reactivity standpoint, HP-2 has the structural capability of acting as both a strong acid and a strong chemical oxidizing agent under propellant cure and storage conditions. Studies of HP-2 compatibility with propellant components have been undertaken in various laboratories in order to clearly define the reactive capability of the oxidizer from the standpoint of propellant processing and handling. It should be noted that the majority of these studies, notably the Midwest Reasearch Institute (MRI) work, were performed with purified HP-2. No evidence was found for the presence of trace impurities (other than HP and perchloric acid) in EPR or mass spectrometric studies.

1. Functional Reactivity of Hp-2

(C) McElroy and Nebgen of the Midwest Research Institute have screened the reactivity of HP-2 with various structural functionalities found in solid propellant systems(7). Their approach consisted of measuring the rates as well as determining the nature of oxidizer-substrate reactions and oxidizer decomposition over a range of temperatures, usually 25, 40, 60, and 80°C. They found that HP-2 acted as an oxidizing agent toward organic substrates, though the reaction became apparent and significant only over a relatively long period of time, usually 2 months. This oxidative behavior of HP-2 becomes important when long-range aging behavior of propellants formulated with HP-2 is considered. Carbon dioxide evolution from hydrocarbon materials indicated approximately 1% reaction (on a mole basis) after approximately two months. Of special significance, the urethane cure linkage was reported to undergo degradation (through what appears to be decarboxylation) when contacted with HP-2 at room temperatures.

(U) Of even greater signigicance to propulsion were the reported non-oxidative reactions of HP-2 since they indicate reactivity characteristic of

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strong acids in an organic system. These are the types of reactions which destroy functional groups during formulation and lead to degradation of mechanical properties under storage conditions. For example, ethers were shown to rearrange in the presence of HP-2 at ambient temperature. Another interesting reaction involved a derivative of polytetramethylene oxide; this material readily evolved tetrahydrofuran at room temperature when mixed with HP-2. In this case, the oxidizer seemed to catalyze a depolymerization to tetramethylene oxide followed by cyclization of the latter. These reactions indicate the possibility of HP-2 causing rearrangements in binder materials containing the ether group.

(U) To further characterize the ether reaction, McElroy and Nebgen tested 1, 4-diethoxybutane with HP-2. After three weeks at ambient temperature, diethyl ether was a definite gas-phase product along with traces of tetrahydrofuran. The ether cleavage reactions may be attributed to the acidic nature of the oxidizers.

(U) The dehydrating ability of HP-2 on an alcohol was demonstrated with ethanol. Diethyl ether was readily evolved from the test sample. Similar results were demonstrated with R45-M, a polymeric alcohol (MW-~2100). Once again, HP-2 was found to be capable of undergoing side reaction with hydroxyl groups present in binder material.

(U) Epoxy compounds were homopolymerized in the presence of HP-2. The ability of the oxidizer to act as an acid catalyst for these reactions was demonstrated over a range of epoxide compounds.

(U) Olefins, as demonstrated with 1-butene, not only homopolymerized but also isomerized in the presence of HP-2. 1-Butene was converted t trans-2-butene after four months with HP-2. Again this behavior can be attributed to the acidic nature of the oxidizer.

(U) Polymers derived from butadiene, such as Telagen CT and R45M, evolved ethylene and methane slowly when mixed with HP-2.

(U) The results from the MRI program indicate that in a hydrocarbon system, HP-2 matrix reactivity becomes an important factor when storage conditions are considered. The non-oxidative reactions of HP-2 with organic substrates are those expected in an acidic, dehydrating medium.

The types of reactions observed (ether rearrangement, ether and alcohol dehydration, epoxide and olefin homopolymerization, decarboxylation) are more likely to be of significance over a long period of time that under curing conditions, although theoretically they are a possible source of curing cycle difficulties. Some specificity can be destroyed in the curing reaction as extraneous reaction products can be introduced into the system during cure. After cure, the prospects are good that propellant physical and mechanical properties will be altered by the various rearrangement reactions which can occur within the matrix.

2. Studies of Model Reaction Systems.

(U) DiMilo of Aerojet-General Corporation has studied the reactivity of HP-2 with model compounds simulating the chemical environment within a propellant(8). Specifically, the compatibility of the oxidizer was determined with isocyanate, aziridine, and epoxy curing systems. The experimental technique entailed the use of GLC to analyze the model cure system at various stages of reaction. This method had the advantage of not only detecting incompatibilities but also determining the nature of the interaction and its effect on the knetics of the overall cure reaction.

(U) Selection of the model compounds was based on establishing a replication of the structural and/or chemical characteristics of the actual propellant binder. The use of GLC as a convenient analytical tool also dictated the requirement that the compounds studied be of relatively low molecular weight, and volatile.

(U) To simulate the Telagen polymer system with its secondary and primary hydroxyl groups and residual unsaturation, DiMilo used 2-octanol, 1-decanol and 1,7-octadiene. For the carboxy-terminated polymer, a combination of 1-nonanoic acid, 2-ethylhexanoic acid and 1,7-octadiene provided the replica. The model curing agents included n-butyl isocyanate, phenyl isocyanate, 2-ethylaziridine and 1,2-epoxycyclohexane. In addition, acetic, propionic, and hexanoic acids were used to further characterize the reactivity effects of the oxidizer on binder ingredients.

(U) GLC analysis showed that the usual curing functionalities for solid propellants were reactive with HP-2. In all cases no more than 33% of the original sample survived an 18-hour period even at room temperature in the presence of HP-2.

(U) In a more complex reaction system, that is, one containing curing agent, prepolymer, oxidizer, and fuel, both epoxide and aziridine functionalities were consumed rapidly by a side reaction. GLC analysis indicated the cure reaction occurred only to a minor degree. The alcohol isocyanate reaction was catalyzed by the presence of HP-2, the rate being sufficiently fast to cause potlife problems in an actual propellant mix. Slower reacting isocyanates did not solve the problem, because the slower the cure reaction, the greater the side reaction occurrence. HP-2 not only destroys the isocyanate but also dehydrates the hydroxy prepolymer (the complete dehydration of 2-octanol in stirred solution with HP-2 was reported to take place in 20 seconds). No compatible curing agent was reported for use with HP-2.

3. Behavior in NF Systems

(U) The chemistry of HP-2 reported thus far has been one of reactivity with most binder ingredients and one of energetic, autocatalytic decomposition. The picture is bad enough when conventional propellant systems (hydrocarbon, aluminized) are considered; for energetic NF formulations, the situation is worse.

(U) Smith and co-worker[9] at MRI have made an extensive study of the compatibility of the HP-2/PBEP system. The experimental approach entailed mixing the test ingredients in sealed tubes and analyzing the reaction products, both gaseous and condensed, by IR, GLC, NMR and EPR.

(C) The problems of combining HP-2 and PBEP in a propellant are magnified by the inherent instability of the latter material. An introductory note to PBEP status, a short discussion of its behavior in a formulation, is in order. Several investigators[4, 9, 10] have examined this propolymer in an attempt to characterize its structure and define its decomposition kinetics.

(C) Dergazarian[10] has reported that the actual PBEP structure varies considerably from the proposed ideal or theoretical configuration.

Elemental and functional group analyses by both Dergazarian(10) and by Hammond and co-workers(4) have shown that pendant groups other than the methylene difluoroamino group exist in the polymer. PBEP composition is also far from ideal in that the polymer consists of fractions of varying molecular weight, structure, and functionality(5, 9, 10, 11).

(C) Samples of PBEP "as received" were shown to have decomposed during shipment and storage(10). Smith and co-workers(9) reported slow evolution of HF and HCN at ambient temperature. PBEP stability was found to decrease with temperature, the range between 55 and 80° C being barely acceptable for processing(9, 10).

(C) Hammond(4) has reported PBEP to decompose by a free-radical-induced reaction. Structural defects, end groups, and impurities in the polymer appear to be the source of decomposition initiation. Decomposition patterns for different molecular weight fractions of the polymer showed significant differences. A similar stability-molecular weight fraction relationship was noted by Smith(9). An initial and rapid evolution of primary decomposition gases (HF, HCN, HNF_2) was observed during initial heating periods at constant, low temperatures (25 to 40° C). The gassing rate then falls off with time and virtually ceases by 80° C. Thereafter gas evolution continues to rise with increasing temperature. He postulated that low molecular-weight fractions, assumed to be less stable than higher ones, are initially decomposed. After their decomposition, the degradation pattern is indicative of "pure" PBEP.

(C) Hammond(4) has calculated an activation energy of 18 Kcal/mole for PBEP decomposition. Compared to other NF polymers, the decomposition mechanism is realtively simple and involves a low activation energy. The temperature threshold is low, at 80° C, and once decomposition begins, its rate of acceleration is slower than, for example, that of P-FABDE.

(C) The incorporation of PBEP in a propellant formulation with an energetic and intrinsically reactive oxidizer such as HP-2 creates serious, and perhaps insurmountable, compatibility problems. Smith and co-workers(9) have studied the interactions of PBEP and HP-2 by infrared spectroscopy, gas chromatography and mass spectrometry. Their IR

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studies have shown a large increase in gas evolution for the PBEP oxidizer system relative to the polymer alone. The gassing is continous and does not follow the same pattern as for PBEP alone. Significant amounts of N_2, CO, NO, CO_2, and N_2O are evolved from the PBEP/HP-2 system at 50° C in a 16-hour period. HP-2 is much more reactive than either HAP or AP under comparable conditions. From other studies, it is known that a PBEP/HP-2 system evolves large amounts of gas even at 40° C. The evolution of CO, CO_2, and N_2O is indicative of oxidative degradation of PBEP by the oxidizer. The presence of N_2 among the products indicates oxidizer degradation along with PBEP decomposition. Figure 1 summarizes this gas evolution data for the PBEP/HP-2 system. The quantities of gas given off by the ingredients alone under comparable conditions are two orders of magnitude smaller. During a 4-day period at 70° C, the gas quantities from the system indicate ~50% loss of oxidizer and 10% decomposition of PBEP. At 40°C the decomposition is 15% for HP-2 and 1% for the polymer.

(C) Smith also used mass spectroscopy to further characterize the HP-2/PBEP reaction. Even at ambient temperature, HF, HCN, HNF_2, ClO_2, NF and HNF were detected as products from the mixture. The decomposition species reached a maximum intensity then decreased to a constant value after approximately 30 min. HF evolution reached a mixmum value at 60° C and remained constant t 100° C. These data are summarized in Figure 2.

(C) The above compatibility data indicate the PBEP/ HP-2 system to be at least two orders of magnitude more reactive than a comparable AP mixture. It is concluded that HP-2 is entirely too reactive to be formulated with a PBEP binder. Decomposition and oxidative degradation of the polymer occur along with loss of oxidizer. The large quantities of released gases and their reactive nature preclude the possibility of curing a PBEP/HP-2 system. Even if such a propellant could be cured, the high degree of reactivity of the energetic components would result in an unacceptably short storage lifetime for the propellant.
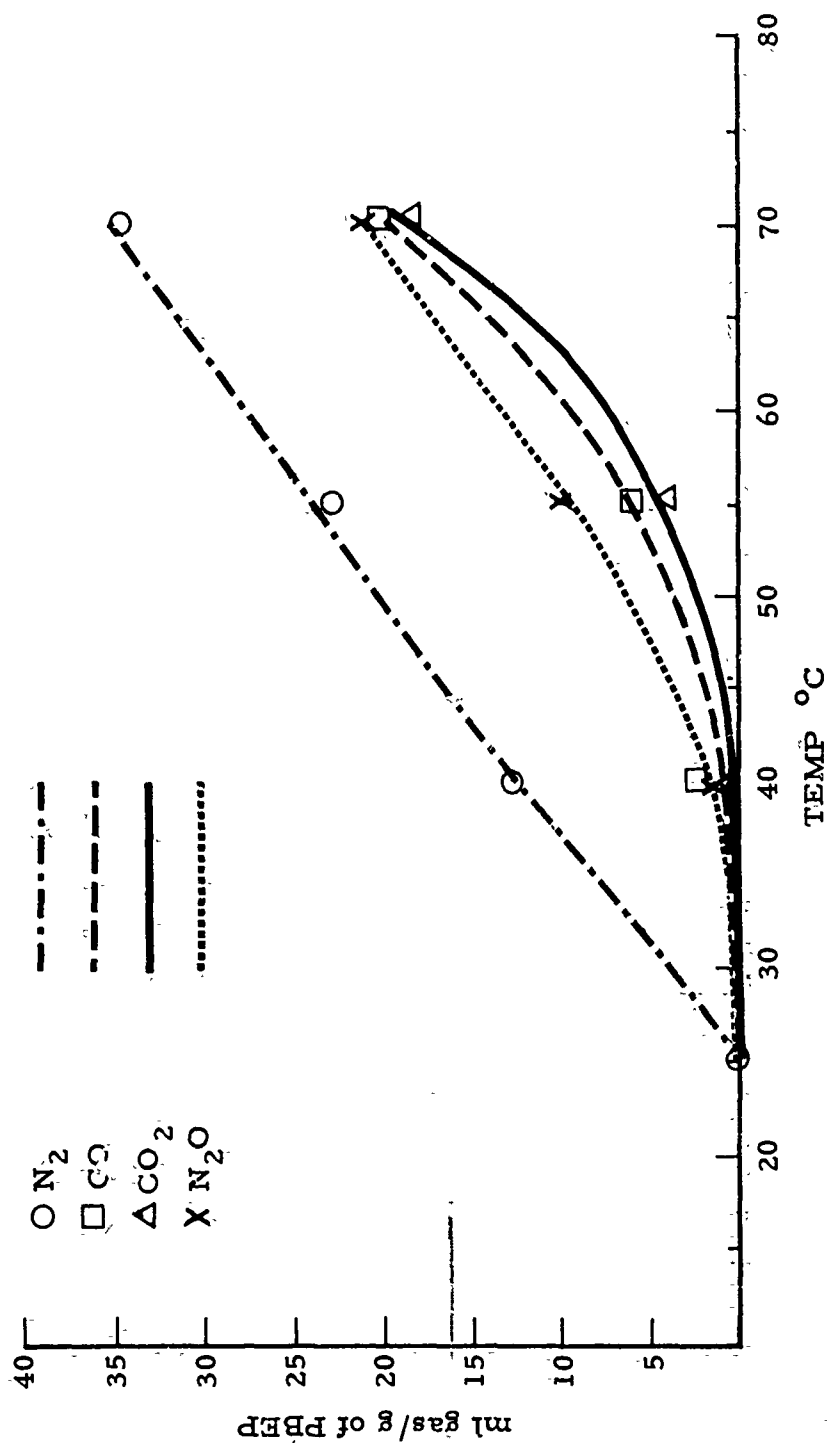
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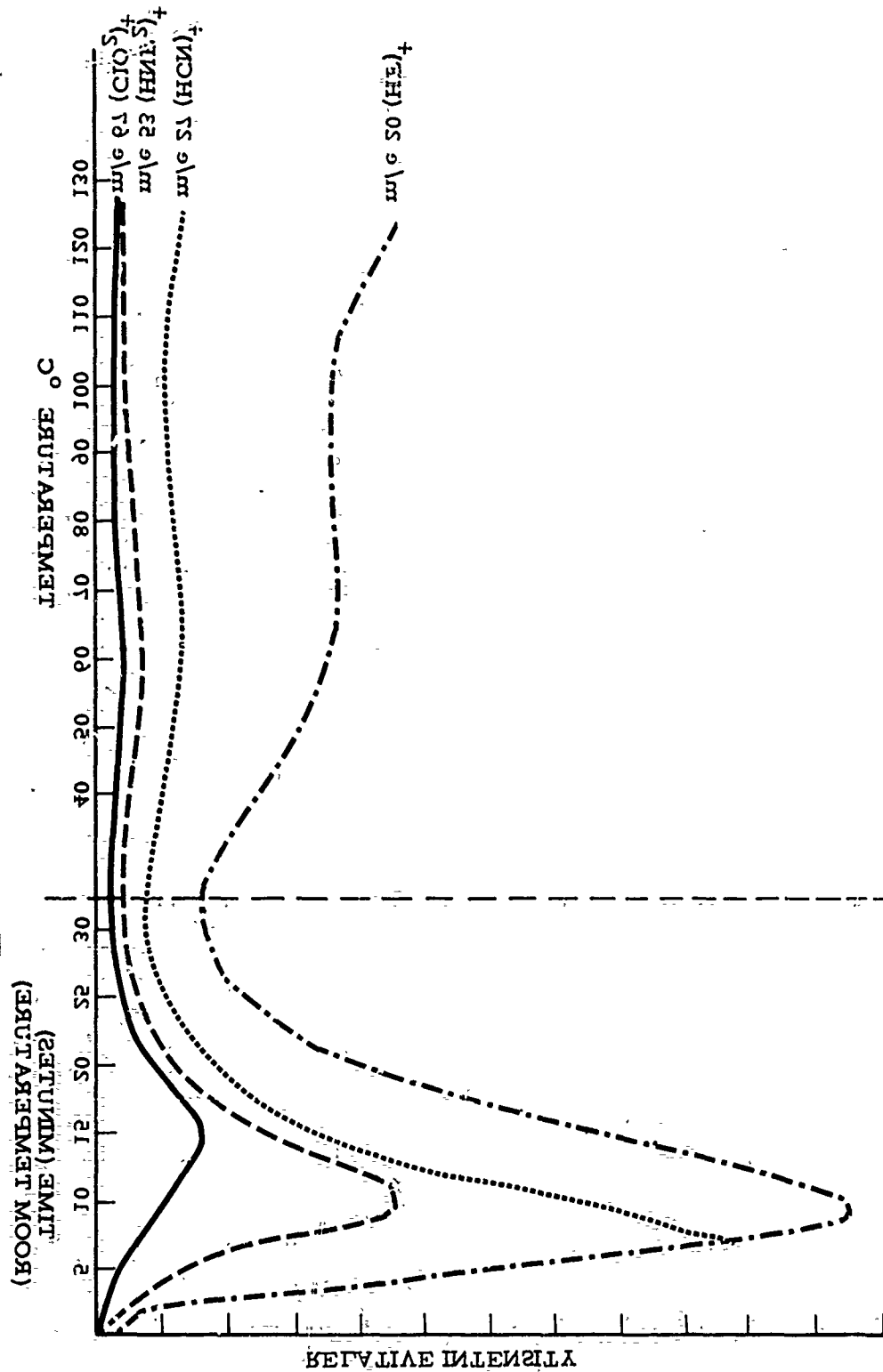Figure 1. PBEP/HP-2 Gaseous Decomposition Products (GLC Analysis - 4 days)

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Figure 2. PBEP/HP-2 System. Mass Spectral Decomposition Pattern For Selected Species.

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SECTION V
DISCUSSION

(U) The preceding chapters have described the results of laboratory experiments designed to define the basic chemical behavior of HP-2 propellant components. A major problem for the propulsion chemist is to provide "before-the-fact" interpretation of such data in terms of overall propellant stability. Or, posing the question in different terms, can the data from previous laboratory compatibility experiments and model compound studies be utilized in the component evaluation process for application and use in a propulsion system? The following is an attempt to show the extrapolation of these data to HP-2 motor behavior.

(C) The fact that HP-2, itself, decomposes in the presence of NF materials should be considered in light of the autocatalytic nature of its thermal decomposition. The observation of ClO_2 in the mass spectrometric studies of the PBEP/HP-2 system indicates that active oxidizing species are being generated in the formulation. The presence of such species with the oxidizer is basic to the initiation and propagation of the autocatalytic decomposition of HP-2. From these data, it can be pref ____ that energetic decomposition of an NF/HP-2 formulation would occur under processing conditions which employ temperatures in the 40 to 60° C range. Indeed, such behavior has been ovserved for HP-2 heated at cure temperatures with PBEP and/or TVOPA after 22 hours (induction period followed by violent decomposition). The requirements for such a prediction include a thorough understanding of the mechanism and kinetics of oxidizer decomposition coupled with in-depth study of the reactions of the two components (in this case examined by mass spectrometric analysis of gaseous decomposition products evolved from the formulation).

(C) The behavior of hydrocarbon/HP-2 propellants must be examined in terms of both HP-2 reactivity and the intermediate species formed during its thermal decomposition. The observed deterioration of the mechanical

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and physical properties of aging HP-2 motors is consistent with the oxidizer-organic binder reactivity data reported herein. Perchloric acid generation (as in HP-2) within an organic matrix will give rise to oxidative degradation of the latter accompanied by enough gas formation to destroy propellant structural integrity. This process is undoubtedly exothermic, hence the propellant is undergoing a self-heating and catalytic reaction series during storage. The uniformity of this effect will be dependent upon the distribution of oxidizer particles through the matrix on a micro scale.

(C) The structure of the binder matrix, the concentration of oxidizer among other solids in a given matrix, and the distribution of potential and reactive additives are variable throughout the propellant (once again, on a micro scale). This variability imposes limitations on the reproducibility of phenomena which depend on aging deterioration for their effect. Hence, the mechanical properties of all HP-2 motors will deteriorate to a certain extent on aging. However, the effect may not be uniform or reproducible.

(C) The increased frequency of saturated (relative to unsaturated) binder motor failures can also be rationalized in terms of oxidizer-binder reactivity. Oxidizer attack on an unsaturated binder leads to oxidative cross-linking, a process in which new bonds are made within the propellant. The saturated system offers oxidative degradation of the backbone as the main reaction route. The latter process thus involves bond cleavage whereas the first, though undesirable also, involves bond formation. The rates of the processes may be different and the oxidative degradation of the saturated backbone may be the more deleterious of the two routes. Hence, structural failure in the saturated system may be more rapid and therefore more noticeable than in the unsaturated system.

(C) The abnormal combustion behavior of HP-2 propellants should be examined in light of the species formed during their decomposition. The formation of hudrazoic acid has been observed under thermal decomposition conditions which simulate those of the combustion process. This material, formed by oxidation of hydrazine, has been appropriately described as "fearfully and dangerously explosive." It is a liquid boiling at 37° C which detonates violently when subjected to shock and reacts with oxidizing

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and reducing agents. The effects of this material (and other materials formed during the HP-2 decomposition process) on combustion phenomena is an area of study which unfortunately has been neglected. The techniques exist (e. g. , flash mass thermal analysis under controlled heating-rate conditions) for such an investigation but resource limitations preclude further work on HP-2. However, for the sake of the completeness of propellant stability theory, brief examination should be given this area.

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SECTION VI
SUMMARY AND CONCLUSIONS

(C) The thermal instability of HP-2 and the resultant effects may be attributed to the ease with which one of its perchloric acid groups is lost. Perchloric acid decomposition (which has a low activation energy) is the rate-determining step in the overall decomposition of the oxidizer. Perchloric acid is also the major source of incompatibility in HP-2 propellant systems. Thus, there is a direct relationship between oxidizer "acidity" and oxidizer thermal instability. At 50° C, oxidizer degradation becomes excessive in a week's time. HP-2 propellants would not survive thermal conditions more severe than those encountered by ballistic missiles.

(C) The question arises: Can HP-2 be stabilized by additive treatment? Most of the data point to a case of intrinsic reactivity for HP-2. It is conceivable that pretreatment of the oxidizer may lend a slight increase in stability, but it appears unlikely that such an increase could be sufficient to render HP-2 usable in a practical propellant system. The fact that pretreatment has increased the stability of practical AP propellants may not necessarily apply to more energetic systems. Ammonium perchlorate is so much more stable than hydrazinium diperchlorate that the extrapolation itself may not be valid or the trade-off between ballistic properties and stability (due to additive concentration) may be too great to render such a propellant cost effective.

(C) In summary, HP-2 is an energetic material which violates most of the fundamental requirements for propellant stability: (1) it is reactive with most propellant components, especially NF containing ingredients; (2) under storage conditions not only does its reactivity degrade the propellant matrix but the oxidizer itself also decomposed, giving rise to materials such as HP, $HClO_4$, and possibly HN_3, all of which are significantly more hazardous than the parent material; (3) its reactivity with NF binders is so great that sucessful formulation is doubtful; (4) any propellant system utilizing it would have a short storage liketime.

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(U) The history of HP-2 propellant development indicates that several key areas useful for predicting propellant behavior have been neglected. This is surprising, since the potential hazard and instability of HP-2 should have been obvious from even the limited data available during the early stages of its evaluation. Techniques exist today for gathering sufficient meaningful data to permit accurate predictions concerning propellant behavior and at least define problem areas. The proper use of these techniques in an integrated ingredient evaluation program can save considerable time and money in an overall propellant development effort--the unsuccessful attempt to utilize HP-2 as a propellant oxidizer is a noteworthy case in point.

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Air Force Rocket Propulsion Labortory Edwards, Calif 93523	CONFIDENTIAL
	2b. GROUP IV

3. REPORT TITLE

A Review of Recent Compatibility and Stability Studies on Hydrazinium Diperchlorate

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Special Report

5. AUTHOR(S) *(First name, middle initial, last name)*

Raymond E. Foscante, Capt, USAF

6. REPORT DATE March p969	7a. TOTAL NO. OF PAGES 30	7b. NO. OF REFS 11
8a. CONTRACT OR GRANT NO. b. PROJECT NO. 3148 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) AFRPL-TR-69-46 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT

In addition to security requirements which must be met, this document is subject to special export controls and each transmittal to foeign governments or foreign nationals may be made only with prior approval of AFRPL(RPORT-STINFO), Edwards, Calif.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Rocket Propulsion Labortory Air Force Systems Command, USAF Edwards, California 93523

13. ABSTRACT

Recent developments in hydrazinium diperchlorate (HP-2) chemistry are reviewed and related to solid propellant behavior. The reactions of HP-2 with model compounds and actual propellant ingredients are discussed with special attention paid to those interactions leading to gas generation, homopolymerization of binder components, oxidizer decomposition, cure reaction inhibition, and cure linkage destruction. The details of studies on the compatibility of HP-2 with NF systems are reviewed and conclusions reported. These fundamental chemical observations are then discussed in terms of large motor behavior.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hydrazinium Diperchlorate						
Solid Propellant Behavior						
Oxidizer						
Compatibility						
Stability						
PBEP						
TVOPA						

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